



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08F 297/04, C08G 81/02 C09J 153/02, 7/02	A1	(11) International Publication Number: WO 92/20725 (43) International Publication Date: 26 November 1992 (26.11.92)
(21) International Application Number: PCT/US92/04334 (22) International Filing Date: 22 May 1992 (22.05.92) (30) Priority data: 705,193 24 May 1991 (24.05.91) US (71) Applicants: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center Abbott Road, Midland, MI 48640 (US). EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77522 (US). (72) Inventors: DIEHL, Charles, F. ; 4828 Front Royal Drive, Baton Rouge, LA 70817 (US). MARCHAND, Gary, R. ; 4028 Lassen Drive, Baton Rouge, LA 70814 (US). MYERS, Michael, O. ; 16716 Bristoe Avenue, Baton Rouge, LA 70816 (US). TANCREDE, Jean, M. ; 936 Shadybrook Drive, Baton Rouge, LA 70816 (US).		(74) Agents: HEWITT, Lester, L. et al. ; Pravel, Gambrell, Hewitt, Kimball & Krieger, 1177 West Loop South, 10th Floor, Houston, TX 77027-9095 (US). (81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC (European patent), MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL (European patent), NO, PL, RO, RU, SD, SE (European patent), SN (OAPI patent), TD (OAPI patent), TG (OAPI patent). Published <i>With international search report.</i>
(54) Title: RADIAL BLOCK COPOLYMERS, HOT MELT ADHESIVE COMPOSITIONS, AND ARTICLES PRODUCED THEREFROM (57) Abstract <p>Radial block copolymers characterized by the formulae: (1) (pS-pI)_nX and (2) (pS-pI-pB)_nX where pS is polystyrene, pI is polyisoprene, pB is butadiene, X is a residue of a multifunctional coupling agent used in the production of the radial block copolymer, and n is a number greater than 2 representative of the number of branches appended to X; hot-melt adhesive compositions constituted of said radial block copolymers, and articles of manufacture produced therefrom. These copolymers possess blocks of high average molecular weight polystyrene (10,000 to 25,000) and an overall average molecular weight (90,000 to 380,000) such that when blended in requisite proportions with a compatible tackifier resin, preferably also a secondary tackifying resin or plasticizing oil, and stabilizer, superior hot-melt adhesive compositions can be formed. The hot-melt adhesive compositions possess, inter alia, superior heat resistance, superior static time to failure with low viscosity, good peel adhesion, good tack, and high ability to bond to a polyethylene or polypropylene substrate at temperatures below that which may damage the substrate.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MI	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

**RADIAL BLOCK COPOLYMERS, HOT MELT ADHESIVES
COMPOSITIONS, AND ARTICLES PRODUCED THEREFROM**

1 **1. Field of the Invention**

2 This invention relates to radial block
3 copolymers, hot-melt adhesive compositions, and
4 articles formed or constructed therefrom. In parti-
5 cular, it relates to radial block copolymers consti-
6 tuted of resinous polystyrene block segments and
7 resinous polydiene block segments, specifically a
8 polyisoprene block or a predominantly polyisoprene
9 block containing polybutadiene, and to improved hot-
10 melt adhesive compositions formed from said block
11 copolymers, especially adhesives of a type useful in
12 the assembly of disposable articles, particularly
13 disposable articles wherein the hot-melt adhesive
14 composition is employed in the construction to bond a
15 polyethylene or polypropylene substrate to a tissue,
16 non-woven fabric or absorbent fluff.

17 **2. Background**

18 It is known to prepare hot-melt adhesive
19 compositions from polystyrene-polyisoprene-
20 polystyrene and polystyrene-polybutadiene-polysty-
21 rene block copolymers. Linear polystyrene-polyiso-
22 prene-polystyrene block copolymers, hot melt adhesive
23 compositions based on these block copolymers,
24 articles produced from these adhesives, are disclosed
25 in U.S. Patent Application Serial No. 393,545.

- 2 -

1 supra. The linear polystyrene-polyisoprene-polysty-
2 rene block copolymer; or linear, pS-pI-pS block
3 copolymer, disclosed by this application is character-
4 ized by any of the formulas: (1) $pI-(pS-pI)_n$,
5 where n is 2, or greater than 2; (2) $pS-(pI-pS)_n$,
6 where n is 1, or greater than 1; or (3) $(pS-pI)_n$,
7 where n is 2, or greater than 2; wherein, in any of
8 formulas (1), (2) or (3), pS is a polystyrene block
9 having an average molecular weight ranging from about
10 12,000 to about 20,000, preferably from about 14,000
11 to about 19,000, pI is a polyisoprene block having an
12 average molecular weight ranging from about 30,000 to
13 about 70,000, preferably from about 35,000 to about
14 60,000, the overall molecular weight of the block
15 copolymer ranges from about 60,000 to about 110,000,
16 preferably from about 70,000 to about 95,000, and the
17 polystyrene block pS components are present in an
18 amount of at least about 27 parts to about 50 parts,
19 preferably from about 35 parts to about 45 parts, per
20 100 parts by weight of the block copolymer. The
21 pS-pI-pS block copolymer, in all embodiments is char-
22 acterized by the presence of a pI block, or polyiso-
23 prene block, located between two pS blocks, or
24 polystyrene blocks which may or may not be terminal
25 endblocks. The pS-pI-pS block copolymer can thus be
26 either a triblock or multi-block copolymer, though
27 the triblock copolymer is preferred.

28 The hot melt adhesive composition is con-
29 stituted of the pS-pI-pS block copolymer, a compati-
30 ble primary tackifier resin, preferably also a
31 secondary tackifier or plasticizing resin or plasti-
32 cizing oil, and stabilizer. These block copolymers,
33 when blended in the requisite proportions with these
34 components, produce adhesives with high shear holding
35 power and shear adhesion failure temperature, and a

- 3 -

1 low overall molecular weight sufficient to provide
2 low viscosity. These adhesives have, inter alia,
3 been found admirably suitable for the construction of
4 disposable articles wherein the adhesive is applied
5 as a continuous or discontinuous phase between
6 members, e.g., via brushing, spraying or air-extru-
7 sion, between members to be bound together, particu-
8 larly disposable articles of multi-line construction
9 wherein the adhesive is supplied as fine parallel
10 longitudinal strips, or as a multi-dot pattern of
11 adhesive droplets, to bond together a moisture
12 impervious outer polyethylene or polypropylene sheet
13 and an inner moisture adsorbent sheet, or tissue, as
14 used in diaper constructions. They have also been
15 found suitable for use in the construction of
16 sanitary napkins, bed pads, and with or without the
17 addition of other materials, are useful for packaging
18 and carton sealing, magazine and book lining, or book
20 binding, or as elastic glues generally.

21 Adhesives formed from this type of pS-pI-pS
22 block copolymer has been found admirably suitable,
23 e.g., in the production of "multi-line" (or multi-
24 dot) constructions. Hot-melt adhesives applied in
25 the form of fine parallel longitudinal strips (or as
26 patterns of dots) have been found to possess suffi-
27 cient adhesive and cohesive strength to provide high
28 bond strength values so that when subjected to stress
29 the constructions cannot be easily separated.
30 Moreover, the adhesives can withstand high mixing and
31 application temperatures without thermal degradation
32 and loss of adhesive properties, and have good heat
33 and oxidation resistance on aging. The adhesives
34 also perform well at moderate temperatures, which is
35 required since the disposable articles are worn at

- 4 -

1 body temperature; and they also perform well at
2 higher temperatures, which is also required since the
3 constructed articles must also be exposed to elevated
4 temperatures during warehousing and shipping.
5 Furthermore, these hot-melt adhesives have low adhe-
6 sive viscosity such that they can be applied at low
7 temperature in order to avoid distortion of the
8 polyethylene or polypropylene substrates to which the
9 adhesive is applied. Nonetheless, there remains a
10 need for hot-melt adhesives useful in magazine and
11 book binding, elastic gluing operations generally,
12 hot-melt adhesive compositions useful in the assembly
13 of multi-line constructions, and disposable articles
14 of multi-line construction formed from improved
15 hot-melt adhesive compositions.

16 3. Objects

17 It is, accordingly, a primary objective of
18 this invention to fulfill these and other needs.

19 A particular object of this invention is to
20 provide novel radial block copolymers constituted of
21 a polystyrene block segment and a polydiene block
22 segment, viz. a polyisoprene block or a polyisoprene
23 block containing some polybutadiene, and improved
24 hot-melt adhesive compositions particularly useful in
25 the assembly of disposable articles of manufacture,
26 particularly disposable articles of multi-line
27 construction, formed from such radial block copoly-
28 mers.

29 A further, and more particular object is to
30 provide hot-melt adhesive compositions which have
31 superior heat resistance, superior static time to
32 failure with low viscosity, good peel adhesion, and
33 good tack and high ability to bond to a polyethylene
34 or polypropylene substrate at temperature below that
35 which would be injurious to the substrate.

- 5 -

1 A further, and yet more specific object is
2 to provide disposable articles as previously des-
3 cribed, particularly disposable articles of multi-
4 line or multi-dot construction, wherein a polyethy-
5 lene or polypropylene substrate is bonded to a
6 tissue, or non-woven polyethylene or polypropylene
7 substrate, or both, via the use of said improved hot-
8 melt adhesive compositions.

9 4. The Invention

10 These objects and others are achieved pur-
11 suant to the practice of this invention, embodying a
12 novel radial block copolymer constituted of resinous
13 polystyrene block segments and resinous polydiene
14 block segments, suitably a polyisoprene block or a
15 predominantly polyisoprene block containing a rela-
16 tively small amount of polybutadiene, and a novel
17 hot-melt adhesive composition comprising said novel
18 copolymer, compatible primary tackifier resin,
19 preferably also a secondary tackifier resin or
20 plasticizing oil, and stabilizer. The hot-melt
21 adhesive composition is, in particular, comprised of
22 said radial block copolymers the polystyrene blocks
23 of which are sufficiently high average molecular
24 weight to provide, inter alia, when blended in the
25 requisite proportions with a compatible tackifier
26 resin, preferably also a secondary tackifier resin or
27 plasticizing oil, and stabilizer, high shear holding
28 power and shear adhesion failure temperature, and a
29 low overall molecular weight sufficient to provide
30 low viscosity.

31 The novel radial polystyrene-polyisoprene
32 or polystyrene-polyisoprene/polybutadiene block
33 copolymer is characterized by the formulas:

- 6 -

1 (1) (pS-pI)_nX

2 (2) (pS-pI-pB)_nX

3 where pS is polystyrene, pI is polyisoprene, pB is
4 polybutadiene, X is a residue of a multifunctional
5 coupling agent used in the production of the radial
6 block copolymer, and n is a number greater than 2,
7 and representative of the number of branches appended
8 to X. The number n, for (pS-pI)_n X block copolymers,
9 will on the average range from above 2 to about
10 6, preferably above about 3 to about 5; and for
11 (pS-pI-pB)_n X block copolymers, on the average will
12 range from above about 3 to about 7, preferably above
13 about 3.5 to about 4. In either formula (1) or (2),
14 pS is a polystyrene block having an average number
15 molecular weight ranging from about 10,000 to about
16 25,000, preferably from about 14,000 to about 20,000,
17 and pI is a polyisoprene block having an average
18 number molecular weight ranging from about 20,000 to
19 about 70,000, preferably from about 20,000 to about
20 40,000. In formula (2), pI-pB is a polyisoprene/
21 polybutadiene block, or polyisoprene block an end of
22 which contains butadiene, or polybutadiene, and the
23 pI-pB component is one having a total average number
24 molecular weight ranging from about 20,000 to about
25 70,000, preferably from about 20,000 to about
26 40,000. The overall number average molecular weight
27 of the radial block copolymer in accordance with
28 either formula (1) or formula (2) ranges from about
29 90,000 to about 380,000, preferably from about
30 100,000 to about 240,000, more preferably
31 from about 120,000 to about 200,000, and the polysty-
32 rene block pS components are present in an amount of
33 at least about 25 parts to about 50 parts, preferably
34 from about 27 parts to about 45 parts, per 100 parts
35 by weight of the radial block copolymer.

- 7 -

1 The radial block copolymers of this in-
2 invention are thus constituted of resinous polysty-
3 rene block segments and resinous polydiene block
4 segments, suitably, in accordance with formula (1),
5 of polyisoprene, pI; or, in accordance with formula
6 (2), of polyisoprene and polybutadiene, pI-pB. Thus,
7 styrene is employed to make the resinous pS block
8 segments of both the $(pS-pI)_nX$ and $(pS-pI-pB)_nX$
9 block copolymers. In accordance with formula (1),
10 isoprene is employed to make the resinous pI block
11 segments, the $(pS-pI)$ polymer chains being formed by
12 sequential polymerization of isoprene with the pS.
13 The $(pS-pI)$ polymer chains, suitably as pS-pI-Li
14 living polymer chains, are coupled with coupling
15 agents possessing at least three, and preferably four
16 sites reactive toward carbon-lithium bonds, e.g.,
17 $SiCl_4$, to form the radial or multiblock $(pS-pI)_nX$
18 copolymer. In forming the radial or multiblock
19 copolymer described by formula (2), i.e.,
20 $(pS-pI-pB)_nX$, pS-pI-pB-Li polymer chains are formed
21 by the sequential polymerization of living pS-pI-Li
22 polymer chains with butadiene. The radial or multi-
23 block $(pS-pI-pB)_nX$ copolymers are correspondingly
24 made by coupling the pS-pI-pB-Li living polymer
25 chains with the multi- or tetra functional coupling
26 agent, e.g., $SiCl_4$. Thus, the styrene is polymer-
27 ized to form pS, the isoprene is then introduced to
28 form pS-pI, the butadiene is then introduced to form
29 pS-pI-pB, and the pS-pI-pB chains are then coupled
30 with the tetrafunctional coupling agent to form the
31 $(pS-pI-pB)_nX$ radial or multiblock polymer. In the
32 pI-pB segment of the $(pS-pI-pB)_nX$ polymer, the
33 polyisoprene is present in amount sufficient to
34 impart predominantly polyisoprene characteristics,
35 not butadiene or polybutadiene characteristics, to

1 the polymer. Thus, in the pI-pB segments of the
2 polymer, the weight amount of polyisoprene will
3 exceed 50 percent of the total weight of diene in the
4 polymer, i.e., $pI/(pI + pB) > 50 \text{ wt.}\%$. Conversely,
5 the weight amount of butadiene or polybutadiene will
6 be less than 50 percent of the total weight of diene
7 in the polymer, i.e., $pB/(pI + pB) < 50 \text{ wt.}\%$.
8 Preferably the polybutadiene portion of the diene
9 segment is less than 10 percent, most preferably less
10 than 5 percent, based on the total weight of the
11 $(pI + pB)$, or diene component of the polymer.

12 The small amount of butadiene at the end of
13 the diene midblock is useful in that it enhances the
14 coupling reaction in formation of the polymer, and
15 results in a radial polymer with a higher number of
16 branches. A further description of the process at
17 this point will facilitate an understanding of this
18 feature of the invention. The radial polymers of
19 this invention are thus synthesized by first contact-
20 ing styrene polymer with an initiator, suitably e.g.,
21 a sec-butyllithium initiator, in the presence of an
22 inert diluent, e.g., cyclohexane. A living polymer
23 is then formed, as represented e.g., by the simpli-
24 fied structure pS-Li. The living polystyrene polymer
25 pS-Li is next contacted with an isoprene monomer;
26 the resulting product being represented by the
27 simplified structure pS-pI-Li. The living polymer is
28 then "coupled" by reacting the pS-pI-Li with a multi-
29 functional coupling agent, or agent which has three
30 or more sites, e.g., $SiCl_4$, to produce a polymer with
31 a radial or branched structure which may be represen-
32 ted as $(pS-pI)_nX$, where X is a residual of the multi-
33 functional coupling agent, and n is a number greater
34 than 2. Alternately, the living polymer pS-pI-Li can
35 be contacted with a small amount of butadiene monomer

- 9 -

1 to produce a living polymer with the structure
2 pS-pI-pB-Li, where pB represents butadiene or
3 polybutadiene. Coupling of the pS-pI-pB-Li with the
4 coupling agent produces a branched block copolymer
5 with the structure (pS-pI-pB)_nX. The radial polymer
6 that is produced, using SiCl₄ as a coupling agent,
7 will on the average produce (pS-pI-pB)_nX polymers
8 where n approximates 4, whereas, in contrast, in
9 producing (pS-pI)_nX polymers in an otherwise similar
10 manner it will be found that n will more closely
11 approximate 3. The butadiene need be added only in
12 amount necessary to assure that the ends of all of
13 the pI segments of the polymer chains are provided
14 with at least one molecule of butadiene, though as
15 suggested the butadiene can be added in larger
16 amounts. The radial block copolymers of this
17 invention, in either event, have been found to pro-
18 duce unexpectedly good hot melt adhesives when com-
19 bined with suitable tackifier resins, plasticizer
20 oils, and antioxidants.

21 Useful coupling agents are those possess-
22 ing three or more, preferably four, sites reactive
23 toward carbon-lithium bonds. Suitable coupling
24 agents are those compositions of the formula X(L)_n
25 where X represents the coupling moiety residue,
26 and L is a suitable leaving group. Exemplary of
27 coupling agents of this type are silica halides,
28 e.g., SiCl₄, or a silane compound where one or more
29 of the halides is substituted by a hydrocarbyl group,
30 e.g., methyl trichlorosilane; epoxy compounds, e.g.,
31 epoxidized linseed oil, epoxidized soybean oil;
32 acrylate multi esters, e.g., pentaerythritol tetra-
33 acrylate; epoxy silanes; divinyl compounds, e.g.,
34 divinyl benzene, and the like.

- 10 -

1 The hot-melt adhesive composition is, in
2 particular, comprised of from about 15 percent to
3 about 35 percent, preferably from about 20 percent to
4 about 30 percent, based on the weight of the hot-melt
6 adhesive composition, of said radial block copolymer
7 wherein the pI component or pI-pB component, respect-
8 tively, is one having an average molecular weight
9 ranging from about 20,000 to about 70,000, preferably
10 from about 20,000 to about 40,000, the pS component
11 is polystyrene having an average molecular weight
12 ranging from about 10,000 to about 25,000, preferably
13 from about 14,000 to about 20,000, the overall
14 molecular weight of the block copolymer ranges from
15 about 90,000 to about 380,000, preferably from about
16 100,000 to about 240,000, and wherein the pS compo-
17 nent is present in an amount of at least about 25
18 parts up to about 50 parts, preferably from about 27
19 parts to about 45 parts, per 100 parts by weight of
20 the radial block copolymer; from about 45 percent to
21 about 70 percent, preferably from about 50 percent to
22 about 60 percent, based on the weight of the hot-melt
23 adhesive composition, of a compatible primary tacki-
24 fying resin; from 0 percent to about 30 percent,
25 preferably from about 5 percent to about 20 percent,
26 of a plasticizing oil, or secondary tackifying resin,
27 or both, based on the weight of the hot-melt adhesive
28 composition; and from about 0.1 percent to about 2
29 percent, preferably from about 0.5 percent to about
30 1.5 percent of a stabilizer, based on the weight of
31 the hot-melt adhesive composition.

- 11 -

1 These hot-melt adhesive compositions, con-
2 stituted of a (pS-pI)_n X or (pS-pI-pB) X radial block
3 copolymer of intermediate to relatively high styrene
4 content and overall low molecular weight to which the
5 primary tackifying resin, the secondary tackifying
6 resin or plasticizing oil, and stabilizer have been
7 added, have been found to possess properties which
8 are admirably suitable for the construction of
9 disposable articles wherein the adhesive is applied
10 as a continuous or discontinuous phase, or substrate,
11 between members, e.g., via brushing, spraying or air-
12 extrusion, between members to be bound together.
13 articles, particularly disposable articles of multi-
14 line construction wherein the adhesive is applied as
15 fine parallel longitudinal strips, swirled, or as a
16 multi-dot pattern of adhesive droplets, to bond
17 together a moisture impervious outer polyethylene or
18 polypropylene sheet and an inner moisture absorbent
19 sheet, or tissue, as used in diaper constructions.
20 These adhesive compositions have also been found
21 suitable for use in the construction of sanitary
22 napkins, bed pads, and, with or without the addition
23 of other materials, are also useful for packaging and
24 carton sealing, magazine and book lining, or book
25 binding, or as elastic glues generally. These hot-
26 melt adhesive compositions can be melted, and
27 maintained under a blanketing nitrogen atmosphere, at
28 relatively low to high temperatures without thermal
29 degradation. The compositions can be applied in
30 fluid form to polyethylene and polypropylene sub-
31 strates as continuous or discontinuous films,
32 suitably as fine lines or as patterns of multi-dots,
33 without any risk of damage to the polyethylene or
34 polypropylene substrate. These hot-melt adhesive
35 compositions have also been found to serve a con-

1 struction function in binding together an outer
2 sheet, or wrapper overlapped with an absorbent pad as
3 required in the construction of sanitary napkins.
4 The hot-melt adhesive composition applied as a fluid
5 permeates the overlapped area to bind and seal the
6 absorbent pad inside the outer sheet which serves as
7 a wrapper.

8 The primary tackifying resins useful in the
9 practice of this invention include hydrocarbon
10 resins, synthetic polyterpenes, rosin esters and
11 natural terpenes which are semi-solid or solid at
12 ambient temperatures, and soften or become liquid at
13 temperatures ranging generally from about 70°C to
14 about 135°C, preferably from about 85°C to about
15 120°C. Exemplary of the primary tackifying resins
16 are compatible resins such as (1) natural and
17 modified rosins such, for example, as gum rosin, wood
18 rosin, tall oil rosin, distilled rosin, hydrogenated
19 rosin, dimerized rosin, and polymerized rosin;
20 (2) glycerol and pentaerythritol esters of natural
21 and modified rosins, such, for example, as the
22 glycerol ester of pale, wood rosin, the glycerol
23 ester of hydrogenated rosin, the glycerol ester of
24 polymerized rosin, the pentaerythritol ester of
25 hydrogenated rosin, and the phenolic-modified
26 pentaerythritol ester of rosin; (3) copolymers and
27 terpolymers of natured terpenes, e.g., styrene/
28 terpene and alpha methyl styrene/terpene; (4)
29 polyterpene resins having a softening point, as
30 determined by ASTM method E28-58T, of from about 80°
31 to 150°C; the latter polyterpene resins generally
32 resulting from the polymerization of terpene hydro-
33 carbons, such as the bicyclic monoterpene known as
34 pinene, in the presence of Friedel-Crafts catalysts
35 at moderately low temperatures; also included are

- 13 -

1 the hydrogenated polyterpene resins; (5) phenolic
2 modified terpene resins and hydrogenated derivatives
3 thereof such, for example, as the resin product
4 resulting from the condensation, in an acidic medium,
5 of a bicyclic terpene and a phenol; (6) aliphatic
6 petroleum hydrocarbon resins having a Ball and Ring
7 softening point of from about 70° to 135°C; the
8 latter resins resulting from the polymerization of
9 monomers consisting primarily of olefins and diole-
10 fins; also included are the hydrogenated aliphatic
11 petroleum hydrocarbon resins; (7) aromatic petroleum
12 hydrocarbon resins, and mixed aromatic and aliphatic
13 paraffin hydrocarbon resins, and the hydrogenated
14 derivatives thereof; (8) aromatic modified alicyclic
15 petroleum hydrocarbon resins and the hydrogenated
16 derivatives thereof; and (9) alicyclic petroleum
17 hydrocarbon resins and the hydrogenated derivatives
18 thereof. The preferred primary tackifying resins for
19 use in the practice of this invention are represented
20 by sub-paragraphs (1), (3) and (7), supra. Suitable
21 secondary tackifying resins are those named species
22 wherein the resin is a liquid at ambient tempera-
23 ture.

24 Various plasticizing oils are useful in the
25 practice of this invention. The plasticizing oil can
26 be used in place of or in combination with the
27 secondary tackifier to reduce viscosity and improve
28 tack properties. Plasticizing oils which have been
29 found useful include olefin oligomers and low molecu-
30 lar weight polymers as well as vegetable and animal
31 oil and their derivatives. The petroleum derived
32 oils which may be employed are relatively high
33 boiling materials containing only a minor proportion
34 of aromatic hydrocarbons (preferably less than 30%
35 and, more particularly, less than 15% by weight of

- 14 -

1 the oil). Alternately, the oil may be totally non-
2 aromatic. The oligomers may be polypropylenes, poly-
3 butenes, hydrogenated polyisoprene, hydrogenated
4 polybutadiene, polypiperylene and copolymers of
5 piperylene and isoprene, or the like having average
6 molecular weights between about 350 and about
7 10,000. Vegetable and animal oils include glyceryl
8 esters of the usual fatty acids and polymerization
9 products thereof.

10 The stabilizer, or antioxidant, used in
11 accordance with the practice of this invention in-
12 cludes high molecular weight hindered phenols and
13 multifunctional phenols such as sulfur and phospho-
14 rous-containing phenols. Hindered phenols are well
15 known to those skilled in the art and may be charac-
16 terized as phenolic compounds which also contain
17 sterically bulky radicals in close proximity to the
18 phenolic hydroxyl group thereof. In particular,
19 tertiary butyl groups generally are substituted onto
20 the benzene ring in at least one of the ortho posi-
21 tions relative to the phenolic hydroxy group. The
22 presence of these sterically bulky substituted radi-
23 cals in the vicinity of the hydroxyl group serves to
24 retard its stretching frequency and, correspondingly,
25 its reactivity; this steric hindrance thus providing
26 the phenolic compound with its stabilizing proper-
27 ties. Representative hindered phenols include:
28 1,3,5-trimethyl 2,4,6-tris (3,5-di-tert-butyl-4-
29 hydroxybenzyl) benzene; pentaerythrityl tetrakis-3
30 (3,5-di-tertbutyl-4-hydroxyphenyl) propionate;
31 n-octadecyl-3,3,5-di-tert-butyl-4-hydroxyphenyl)-
32 propionate; 4,4'-methylenbis (2,6-tert-butylphenol);
33 4,4'-thiobis (6-tert-butyl-o-cresol); 2,6-di-tert-
34 butylphenol; 6-(4-hydroxyphenoxy)-2,4-bis(n-octyl-
35 thio)-1,3,5 21 triazine; di-n-octadecyl 3,5-di-tert-

- 15 -

1 butyl-4-hydroxy-benzylphosphonate; 2-(n-octylthio)
2 ethyl 3,5-di-tert-butyl-4-hydroxy-benzoate; and
3 sorbitol [hex 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-
4 propionate.]

5 The hot-melt adhesive composition is pre-
6 pared for use by blending the radial block copolymer
7 with the primary tackifying resin, the secondary
8 tackifying resin or plasticizing oil, and stabilizer,
9 in any order or sequence, or these materials can be
10 added together simultaneously to form the adhesive
11 composition. In commercial practice it would be
12 expected that the primary tackifying resin and
13 copolymer, with or without the simultaneous addition
14 of the secondary tackifying resin or plasticiz-
15 ing oil, and stabilizer, would be blended together
16 at sufficiently elevated temperature to form a fluid
17 melt. For example, the copolymer can be blended with
18 the solid compatible primary tackifying resin at
19 temperatures ranging from about 130°C to about 200°C,
20 preferably at from about 150°C to about 180°C, to
21 form a fluid melt. The secondary liquid tackifying
22 resin, or plasticizing oil, and stabilizer, can then
23 be added to the melt. Alternatively, the fluid melt
24 can be prepared with all components of the adhesive
25 composition present ab initio.

26 The following non-limiting examples, and
27 comparative demonstrations, bring out the more
28 salient features of the invention. All parts are
29 given in terms of weight units except as may other-
30 wise be indicated.

1 Examples

2 In conducting the following tests the com-
3 position and properties of the neat radial, and
4 linear block copolymers which were prepared for
5 making the adhesive compositions were determined by
6 techniques "a," "b" and "c". In evaluating the
7 performance characteristics of the adhesive composi-
8 tions produced from the radial, and linear block
9 copolymers test procedures "d" through "f" were
10 employed, to wit:

11 a. Styrene content - of the experimental
12 radial, and linear block copolymers was determined
13 from the proton nmr spectra. Samples were dissolved
14 in a mixture of deuterated tetrachloroethane/
15 tetrachloroethylene, and analyzed on a Bruker 90 MHz
16 spectrometer. Styrene content was calculated from
17 the spectra by the method of V. D. Mochel, Rubber
18 Chem. and Tech., 34 40, 1200 (1967).

19 b. Molecular Weight - of the experimental
20 radial, and linear block copolymers was determined by
21 GPC, using the method described by J. R. Runyon, et
22 al, J. Polym. Sci. 13, 2359 (1969).

23 c. Melt Flow Rate (MFR) - of the experi-
24 mental radial, and linear block copolymers was
25 determined according to ASTM method D-1238-82, using
26 condition "G" (200°C, 5 Kg weight).

27 d. Adhesive Melt Viscosity (ASTM D-3236)
28 - Melt viscosities were measured at a temperature of
29 130°C, using a Brookfield Thermosel viscometer. Low
30 adhesive viscosities are a necessity for processing
31 in multi-line, spray, and fiberization equipment. In
32 addition, the viscosity must be low at relatively low
33 processing temperatures in order to avoid distortion
34 of the polyolefin backing when hot adhesive is
35 applied.

- 17 -

1 e. Shear Adhesion Failure Temperature
2 (SAFT) - is a measure of the ability of the bond to
3 withstand an elevated temperature rising at 10°F/15
4 min., under a constant force which pulls the bond in
5 the shear mode. Bonds 1 inch by 1 inch were formed
6 of adhesive, on a Mylar (polyester) backing, to a
7 stainless steel panel, using a 4.5 lb. rubber
8 roller. The panel was suspended vertically in an
9 oven at 32°C, and allowed to come to equilibrium. A
10 1 kg weight was suspended from the free end of the
11 adhesive tape, and the temperature was raised at
12 10°F/15 min. The temperature at which the tape and
13 weight fell from the panel was recorded. SAFT was
14 reported as the average of three such determina-
15 tions. Adhesives possessing high failure tempera-
16 tures are essential for the assembly of disposable
17 articles, which are often subjected to very high
18 temperatures during storage and shipping. In
19 addition, these articles are used (worn) at body
20 temperature.

21 f. Shear Holding Power (Static Time to
22 Failure Bond Test) - The cohesive strength of the ad-
23 hesives was determined according to the general pro-
24 cedures outlined in PSTC-7 and ASTM D-3654. A 1
25 inch by 0.5 inch bond was applied to a stainless
26 steel panel with a 4.5 lb rubber roller. The plate
27 was suspended vertically and allowed to equilibrate
28 at 35°C. A 1 Kg weight was suspended from the free
29 end of the tape. The time at which the tape and
30 weight fell from the panel was recorded. The shear
31 hold (in min) was reported as the average of four
32 such determinations. Long failure times are desir-
33 able, since they indicate strong bonds, which are
34 essential in certain areas of the disposable con-

- 18 -

1 structions, which are subjected to considerable
2 stress during use.

3 Examples 1-4, which immediately follow,
4 describe the synthesis, and certain characteristics
5 of the (pS-pI-pB)_nX radial polymers of this inven-
6 tion. Examples 5-7, on the other hand, describe the
7 synthesis and certain characteristics of the
8 (pS-pI)_nX radial polymers of this invention. Demon-
9 stration 9 is a linear pS-pI-pS linear block copoly-
10 mer of the type described in Application Serial No.
11 393.545, supra; the performance of which when made
12 into an adhesive is substantially equivalent to that
13 of the radial block copolymers of this invention.
14 Demonstration 8 is a radial styrene-butadiene block
15 copolymer which has a styrene content comparable to
16 that of the copolymers of this invention, but an
17 adhesive produced therefrom has a SAFT performance
18 which is inferior to the radial polymers of this
19 invention. Additionally, for comparative purposes,
20 Demonstrations 10-12 represent polymers obtained from
21 commercial sources, formulated into adhesive composi-
22 tions, and tested. Demonstration 10 thus describes
23 the performance characteristics of an adhesive com-
24 position formed from a radial polystyrene-
25 polybutadiene copolymer produced by Shell Chemical
26 Company; Demonstration 11 an adhesive composition
27 formulated from a linear multiblock polystyrene-
28 polybutadiene copolymer produced by Firestone Tire
29 and Rubber Company; and Demonstration 12 an adhesive
30 composition formed from a linear polystyrene-polyiso-
31 prene-polystyrene copolymer produced by Enichem
32 Americas, Inc.

- 19 -

1 The preparation of the block copolymers,
2 and certain characteristics of the block copolymers,
3 as employed in Examples 1 through 7 and Demonstra-
4 tions 8 and 9 are given as follows:

5 Example 1 (5145-45)

6 To a 5-gallon, stirred reactor under a
7 nitrogen atmosphere were added 12.6 kg of cyclohexane
8 and 905 g of styrene. The temperature of the reactor
9 was brought to 50°C and 147 g of a 0.28 M solution
10 of sec-butyllithium in cyclohexane was added.
11 Polymerization was allowed to continue for 50
12 minutes. The reaction mixture was cooled to 50°C and
13 1148 g of isoprene was added. The isoprene was
14 allowed to polymerize for 32 minutes during which the
15 reaction temperature reached a maximum of 68°C. At
16 the end of the 32 minutes, 34 g of butadiene was
17 added and it was allowed to polymerize for an
18 additional 30 minutes. Then 14 g of SiCl₄ was added
19 slowly over the course of 11 minutes. The reaction
20 was allowed to continue for another 15 minutes before
21 an excess of isopropanol was added to the reaction
22 mixture to quench any residual Li alkyl. A hindered
23 phenol antioxidant was added to the polymer solution
24 which was then devolatilized in a vacuum oven under
25 nitrogen at 100°C for 3 hours.

26 Size exclusion chromatography of the
27 resultant polymer showed two peaks, a high molecular
28 weight peak which was the radial or star shaped
29 polymer comprising 78% of the total polymer and a
30 lower molecular weight peak, comprising 22% of the
31 total polymer, which was the diblock building block
32 before coupling the chain ends using SiCl₄. From
33 gel-permeation chromatography, GPC, it was estimated
34 that each arm of the radial polymer was composed of a
35 polystyrene block of 18,000 molecular weight and

- 20 -

1 22,800 molecular weight polydiene. The melt flow
2 rate was 61.8. Ultimate tensile of the material was
3 2763 psi.

4 Example 2 (5146-14)

5 To a 5-gallon, stirred reactor under a ni-
6 trogen atmosphere were added 12.6 kg of cyclohexane
7 and 718 g of styrene. The temperature of the reactor
8 was brought to 50°C and 134.6 g of a 0.317 M solution
9 of sec-butyllithium in cyclohexane was added. Poly-
10 merization was allowed to continue for 60 minutes.
11 The reaction mixture was cooled to 50°C and 1328 g of
12 isoprene was added. The isoprene was allowed to
13 polymerize for 25 minutes during which the reaction
14 temperature reached a maximum of 77°C. At the end of
15 the 25 minutes, 34 g of butadiene was added and it
16 was allowed to polymerize for an additional 18
17 minutes. Then 13 g of SiCl₄ was added slowly over
18 the course of 6 minutes. The reaction was allowed to
19 continue for another 19 minutes before an excess of
20 isopropanol was added to the reaction mixture to
21 quench any residual Li alkyl. A hindered phenol
22 antioxidant was added to the polymer solution which
23 was then devolatilized in a vacuum oven under
24 nitrogen at 100°C for 3 hours.

25 Size exclusion chromatography of the
26 resultant polymer showed two peaks, a high molecular
27 weight peak which was the radial or star shaped
28 polymer comprising 86% of the total polymer and a
29 lower molecular weight peak, comprising 14% of the
30 total polymer, which was the diblock building block
31 before coupling the materials using SiCl₄. From the
32 GPC it was estimated that each arm of the radial
33 polymer was composed of a polystyrene block of 16,560
34 molecular weight and 30,620 molecular weight poly-
35 diene. The melt flow rate was 18.7. Ultimate

- 21 -

1 tensile of the material was 4430 psi.

2 Example 3 (5146-13)

3 To a 5-gallon, stirred reactor under a ni-
4 trogen atmosphere were added 12.6 kg of cyclohexane
5 and 970 g of styrene. The temperature of the reactor
6 was brought to 50°C and 139.0 g of a 0.317 M solution
7 of sec-butyllithium in cyclohexane was added. Poly-
8 merization was allowed to continue for 88 minutes.
9 The reaction mixture was cooled to 50°C and 1086 g of
10 isoprene was added. The isoprene was allowed to
11 polymerize for 39 minutes during which the reaction
12 temperature reached a maximum of 66°C. At the end of
13 the 39 minutes, 34 g of butadiene was added and it
14 was allowed to polymerize for an additional 33
15 minutes. Then 13 g of SiCl_4 was added slowly over
16 the course of 8 minutes. The reaction was allowed to
17 continue for another 18 minutes before an excess of
18 isopropanol was added to the reaction mixture to
19 quench any residual Li alkyl. A hindered phenol
20 antioxidant was added to the polymer solution which
21 was then devolatilized in a vacuum oven under
22 nitrogen at 100°C for 3 hours.

23 Size exclusion chromatography of the
24 resultant polymer showed two peaks, a high molecular
25 weight peak which was the radial or star shaped
26 polymer comprising 87% of the total polymer and a
27 lower molecular weight peak, comprising 13% of the
28 total polymer, which was the diblock building block
29 before coupling the materials using SiCl_4 . From the
30 GPC it was estimated that each arm of the radial
31 polymer was composed of a polystyrene block of 20,960
32 molecular weight and 23,440 molecular weight poly-
33 diene. The melt flow rate was 29.4. Ultimate
34 tensile of the material was 3316 psi.

- 22 -

1 Example 4 (5146-16)

2 To a 5-gallon, stirred reactor under a ni-
3 trogen atmosphere were added 12.6 kg of cyclohexane
4 and 851 g of styrene. The temperature of the reactor
5 was brought to 50°C and 121.8 g of 0.317 M solution
6 of sec-butyllithium in cyclohexane was added.
7 Polymerization was allowed to continue for 54
8 minutes. The reaction mixture was cooled to 50°C and
9 1200 g of isoprene was added. The isoprene was
10 allowed to polymerize for 31 minutes during which the
11 reaction temperature reached a maximum of 74°C. At
12 the end of the 31 minutes, 34 g of butadiene was
13 added and it was allowed to polymerize for an
14 additional 20 minutes. Then 12 g of SiCl₄ was added
15 slowly over the course of 6 minutes. The reaction
16 was allowed to continue for another 16 minutes before
17 an excess of isopropanol was added to the reaction
18 mixture to quench any residual Li alkyl. A hindered
19 phenol antioxidant was added to the polymer solution
20 which was then devolatilized in a vacuum oven under
21 nitrogen at 100°C for 3 hours.

22 Size exclusion chromatography of the
23 resultant polymer showed two peaks, a high molecular
24 weight peak which was the radial or star shaped
25 polymer comprising 87% of the total polymer and a
26 lower molecular weight peak, comprising 13% of the
27 total polymer, which was the diblock building block
28 before coupling the materials using SiCl₄. From the
29 GPC it was estimated that each arm of the radial
30 polymer was composed of a polystyrene block of 20,730
31 molecular weight and 29,200 molecular weight poly-
32 diene. The 20 melt flow rate was 21.9. Ultimate
33 tensile of the material was 3500 psi.

- 23 -

1 Example 5 (5280-18)

2 To a 5-gallon, stirred reactor under a ni-
3 trogen atmosphere were added 12.6 kg of cyclohexane
4 and 901 g of styrene. The temperature of the reactor
5 was brought to 50°C and 129.2 g of a 0.317 M solution
6 of sec-butyllithium in cyclohexane was added. Poly-
7 merization was allowed to continue for 55 minutes.
8 The reaction mixture was cooled to 50°C and 1147.1 g
9 of isoprene was added. The isoprene was allowed to
10 polymerize for 31 minutes during which the reaction
11 temperature reached a maximum of 69°C. At the end of
12 the 31 minutes, 23.7 g of SiCl_4 was added slowly over
13 the course of 6 minutes. The reaction was allowed to
14 continue for another 30 minutes before an excess of
15 isopropanol was added to the reaction mixture to
16 quench any residual Li alkyl. A hindered phenol
17 antioxidant was added to the polymer solution which
18 was then devolatilized in a vacuum oven under
19 nitrogen at 100°C for 3 hours.

20 Size exclusion chromatography of the
21 resultant polymer showed two peaks, a high molecular
22 weight peak which was the radial or star shaped
23 polymer comprising 82.2% of the total polymer and a
24 lower molecular weight peak, comprising 17.8% of the
25 total polymer, which was the diblock building block
26 before coupling the materials using SiCl_4 . From the
27 GPC it was estimated that each arm of the radial
28 polymer was composed of a polystyrene block of 21,021
29 molecular weight and 26,755 molecular weight polyiso-
30 prene. The melt flow rate was 8.1 g/10 minutes.
31 Ultimate tensile of the material was 3620 psi.

- 24 -

1 Example 6 (5280-19)

2 To a 5-gallon, stirred reactor under a ni-
3 trogen atmosphere were added 12.6 kg of cyclohexane
4 and 714.8 g of styrene. The temperature of the reac-
5 tor was brought to 50°C and 111.7 g of a 0.317 M
6 solution of sec-butyllithium in cyclohexane was
7 added. Polymerization was allowed to continue for 53
8 minutes. The reaction mixture was cooled to 50°C and
9 1327.4 g of isoprene was added. The isoprene was
10 allowed to polymerize for 41 minutes during which the
11 reaction temperature reached a maximum of 74°C. At
12 the end of the 41 minutes, 20.5 g of SiCl₄ was added
13 slowly over the course of 6 minutes. The reaction
14 was allowed to continue for another 30 minutes before
15 an excess of isopropanol was added to the reaction
16 mixture to quench any residual Li alkyl. A hindered
17 phenol antioxidant was added to the polymer solution
18 which was then devolatilized in a vacuum oven under
19 nitrogen at 100°C for 3 hours.

20 Size exclusion chromatography of the
21 resultant polymer showed two peaks, a high molecular
22 weight peak which was the radial or star shaped
23 polymer comprising 78.7% of the total polymer and a
24 lower molecular weight peak, comprising 21.3% of the
25 total polymer, which was the diblock building block
26 before coupling the materials using SiCl₄. From the
27 GPC it was estimated that each arm of the radial
28 polymer was composed of a polystyrene block of 19,138
29 molecular weight and 35,541 molecular weight polyiso-
30 prene. The melt flow rate was 5.7 g/10 minutes.
31 Ultimate tensile of the material was 4210 psi.

- 25 -

1 Example 7 (5280-20)

2 To a 5-gallon, stirred reactor under a ni-
3 trogen atmosphere were added 12.6 kg of cyclohexane
4 and 964.2 g of styrene. The temperature of the
5 reactor was brought to 50°C and 118.5 g of a 0.317 M
6 solution of sec-butyllithium in cyclohexane was
7 added. Polymerization was allowed to continue for 53
8 minutes. The reaction mixture was cooled to 50°C and
9 1087.3 g of isoprene was added. The isoprene was
10 allowed to polymerize for 35 minutes during which the
11 reaction temperature reached a maximum of 69°C. At
12 the end of the 35 minutes, 21.8 g of SiCl₄ was added
13 slowly over the course of 6 minutes. The reaction
14 was allowed to continue for another 32 minutes before
15 an excess of isopropanol was added to the reaction
16 mixture to quench any residual Li alkyl. A hindered
17 phenol antioxidant was added to the polymer solution
18 which was then devolatilized in a vacuum oven under
19 nitrogen at 100°C for 3 hours.

20 Size exclusion chromatography of the
21 resultant polymer showed two peaks, a high molecular
22 weight peak which was the radial or star shaped
23 polymer comprising 84.8% of the total polymer and a
24 lower molecular weight peak, comprising 15.2% of the
25 total polymer, which was the diblock building block
26 before coupling the materials using SiCl₄. From the
27 GPC it was estimated that each arm of the radial
28 polymer was composed of a polystyrene block of 24,534
29 molecular weight and 27,666 molecular weight polyiso-
30 prene. The melt flow rate was 8.9 g/10 minutes.
31 Ultimate tensile of the material was 3340 psi.

- 26 -

1 Demonstration 8 (5145-49)

2 To a 5-gallon, stirred reactor under a ni-
3 trogen atmosphere were added 12.5 kg of cyclohexane
4 and 911.6 g of styrene. The temperature of the
5 reactor was brought to 50°C and 170.8 g of a 0.317 M
6 solution of sec-butyllithium in cyclohexane was
7 added. Polymerization was allowed to continue for 46
8 minutes. The reaction mixture was cooled to 50°C and
9 1123 g of butadiene was added. The butadiene was
10 allowed to polymerize for 46 minutes during which the
11 reaction temperature reached a maximum of 69°C. At
12 the end of the 46 minutes, 21.5 g of SiCl₄ was added
13 slowly over the course of 10 minutes. The reaction
14 was allowed to continue for another 17 minutes before
15 an excess of isopropanol was added to the reaction
16 mixture to quench any residual Li alkyl. A hindered
17 phenol antioxidant was added to the polymer solution
18 which was then devolatilized in a vacuum oven under
19 nitrogen at 100°C for 3 hours.

20 Size exclusion chromatography of the
21 resultant polymer showed two peaks, a high molecular
22 weight peak which was the radial or star shaped
23 polymer comprising 76.3% of the total polymer and a
24 lower molecular weight peak, comprising 23.7% of the
25 total polymer, which was the diblock building block
26 before coupling the materials using SiCl₄. From the
27 GPC it was estimated that each arm of the radial
28 polymer was composed of a polystyrene block of 15,635
29 molecular weight and 19,264 molecular weight polybut-
30 adiene. The melt flow rate was 28.8 g/10 minutes.

- 27 -

1 Demonstration 9 (5054-30)

2 To a 2.6 liter reactor were charged 1499 g
3 of cyclohexane and 85.8 g of styrene monomer. The
4 mixture was heated to 60°C and 7.8 ml of a 0.70 molar
5 solution of sec-butyllithium initiator in cyclohexane
6 was added. After 41 minutes, the reaction tempera-
7 ture was reduced to 58°C and 118.5 grams of isoprene
8 was added. After 39 minutes the living styrene-
9 isoprene diblock polymer was coupled to form a linear
10 styrene-isoprene-styrene triblock polymer by adding
11 32 ml of 0.12 M 1,2-dibromoethane in cyclohexane over
12 a period of 11 minutes. A hindered phenol antioxi-
13 dant was added to the polymer solution which was then
14 devolatized in a vacuum oven under nitrogen at 100°C
15 for 3 hours.

16 Size exclusion chromatography of the resul-
17 tant polymer showed two peaks, a high molecular
18 weight peak which was the linear triblock polymer
19 comprising 86.5% of the total polymer and a lower
20 molecular weight peak, comprising 13.5% of the total
21 polymer, which was the diblock building block before
22 coupling the chain ends using DBE. From the GPC it
23 was estimated that the molecular weight of the
24 styrene blocks was 16,660, and the molecular of the
25 polyisoprene midblock was 42,580. The melt flow rate
26 was 50 g/10 minutes.

27 Adhesive compositions were prepared by com-
28 bining 100 parts of the block copolymer, 220 parts of
29 the primary tackifying resin (Zonatac 105L, available
30 from Arizona Chemical), 80 parts of Tufflo 6056
31 (a plasticizer oil available from Lyondell Petroleum
32 Company), and 3 parts of Irganox 1010 (a stabilizer
33 available from Ciba-Geigy), to produce a homogeneous
34 adhesive blend. The adhesive was coated on 2 mil

- 28 -

1 thick Mylar (polyester) backing, to produce a 1.5 mil
2 thick film, of adhesive.

3 The performance characteristics of the ad-
4 hesives of the block copolymers are given in the
5 Table, the adhesive formulations for the
6 $(pS-pI-pB)_nX$ and $(pS-pI)_nX$ radial block copolymers,
7 or "rubbers" of this invention, designated as
8 Examples 1 through 7, being set out for comparison
9 with adhesive formulations prepared from rubbers not
10 of this invention, i.e., Demonstrations 8-12.
11 Columns 1 and 2 of the Table identifies the specific
12 test run and type of rubber tested. Columns 3-6
13 identifies the MFR, or Melt Flow Rate, the total wt.%
14 styrene content of the rubber, the molecular weight
15 of the polystyrene block component of a rubber, pS,
16 and the molecular weight of the polyisoprene block
17 component of a rubber, pI. Columns 7-9 describe the
18 results of the tests conducted on each of the
19 adhesive formulations, viz. the adhesive viscosity,
20 SAFT, and the holding power. It is clear that the
21 adhesive compositions of this invention, i.e.,
22 Examples 1-7, exhibit superior SAFT (high temperature
23 resistance), and superior holding power (static time
24 to failure).

Table

ADHESIVE FORMULATION:

RUBBER	TYPE	MFR	WT % STYRENE	POLYSTYRENE		POLYDIENE (pD)		ADHES. VISC. 130 C. (CPS)	SAFT (C)	35 C HOLD (MIN)
				NOL WT	MOL WT	NOL WT	MOL WT			
EXAMPLE 1	(pS-pI-pB)n-X	61.8	44.1	18006	22823			7538	83.6	>4000
EXAMPLE 2	(pS-pI-pB)n-X	18.7	35.1	16561	30621			7425	80.4	>4000
EXAMPLE 3	(pS-pI-pB)n-X	29.4	47.2	20955	23441			17425	88.7	>4000
EXAMPLE 4	(pS-pI-pB)n-X	40.3	41.5	20726	29216			13325	88.1	>4000
EXAMPLE 5	(pS-pI)n-X	8.1	45.3	21021	26755			14425	84.4	>4000
EXAMPLE 6	(pS-pI)n-X	5.7	35.3	19138	35541			18700	80.9	>4000
EXAMPLE 7	(pS-pI)n-X	8.9	47.1	24534	27666			17500	88.6	>4000
DEMONSTRATION 8	(pS-pB)n-X	28.8	44.8	15635	19264			9050	76.8	>4000
DEMONSTRATION 9	pS-pI-pS	50	43.9	16660	42580			8875	83.2	>4000
DEMONSTRATION 10 (KRATON DI122)	(pS-pB)n-X	3.3	39.7	14211	21585			15350	72.6	>4000
DEMONSTRATION 11 (STEREON 840A)	(pS-pB)n-PS	12.4	42.3					9575	68.3	453
DEMONSTRATION 12 (EUROPRENE SOLT193B)	pS-pI-pS	12.8	24.2	13189	82622			7650	68.7	395

LEGEND:

pS = POLYSTYRENE BLOCK
 pI = POLYISOPRENE BLOCK
 pB = POLYBUTADIENE BLOCK
 pD = POLYDIENE BLOCK = (pI+pB)

NOTES:

- (1) KRATON is a trademark of Shell Chemical Company
- (2) STERON is a trademark of Firestone Tire and Rubber Company
- (3) EUROPRENE is a trademark of Enichem Americas, Inc.

1 Continuing reference to the Table, Examples
2 1 through 7 show the performance of adhesive composi-
3 tions prepared from radial block polymers whose %
4 styrene, polystyrene molecular weight, and polydiene
5 molecular weight are all within the preferred ranges
6 of the radial block copolymer required for the
7 practice of this invention. It is required that all
8 of these parameters fall within the ranges expressed
9 in order to obtain this superior adhesive perfor-
10 mance. Comparative Example 8, showing the perfor-
11 mance characteristics of an adhesive composition of a
12 radial styrene-butadiene copolymer not of this inven-
13 tion, albeit the copolymer has a styrene content and
14 melt flow rate comparable to the radial copolymers of
15 this invention, is inadequate. Its shear adhesion
16 failure temperature, SAFT, is very poor. Styrene-
17 isoprene copolymers have inherently lower viscosity
18 than styrene-butadiene copolymers of the same
19 molecular weight, and hence the styrene-isoprene
20 copolymers are superior in that they can be made with
21 higher molecular weight pS blocks. As a result, the
22 styrene-isoprene copolymers can be produced with
23 greater SAFT. Comparative Example 9 shows the per-
24 formance characteristics of an adhesive composition
25 made from a linear pS-pI-pS copolymer as disclosed in
26 Application Ser. No. 393,545, supra. Demonstrations
27 10, 11 and 12 represent adhesive compositions
28 prepared from commercially available copolymers
29 having properties which fall outside those require-
30 ments which are necessary to obtain superior hot-melt
31 adhesives, i.e., a radial (pS-pB)_nX block copolymer
32 as represented by Demonstrations 10 (Kraton D 1122),
33 a (pS-pB)_n pS linear multiblock copolymer as repre-
34 sented by Demonstration 11 (Stereon 34 840A), and a
35 linear pS-pI-pS block copolymer as represented by

- 31 -

1 Demonstration 12 (Europrene SOL T 193 B). As shown
2 by the Table, the adhesive compositions of Examples 1
3 through 7 clearly exhibit the best combination of low
4 adhesive viscosity, high SAFT, and high 35°C Hold.

5 A prepared adhesive composition useful for
6 magazine or book binding can also be formed from the
7 hot-melt adhesive composition of this invention by
8 the further addition to the hot-melt adhesive compo-
9 sition of from 0 to about 5 percent, preferably from
10 about 0.5 to about 5 percent, based on the weight of
11 the hot-melt adhesive composition, of a hydrocarbon
12 or petroleum derived wax. Exemplary petroleum
13 derived waxes are, e.g., paraffin and microcrystal-
14 line waxes having melting points within a range of
15 from about 55°C to about 110°C, as well as low
16 molecular weight polyethylene and Fischer-Tropsch
17 waxes.

18 It is apparent that various modifications and
19 changes can be made without departing the spirit and
20 scope of the invention.

21 Having described the invention, what is claimed
22 is:

- 32 -

1 1. A composition of matter useful in forming
2 hot-melt adhesives which comprises
3 a radial block copolymer constituted of a
4 polystyrene block segment and a polyisoprene block
5 segment, or polyisoprene block segment an end of
6 which is constituted of butadiene, as characterized
7 by either of the formulas:

8 (1) $(pS-pI)_nX$, or

9 (2) $(pS-pI-pB)_nX$

10 where pS is polystyrene, pI is polyisoprene, pB is
11 polybutadiene, X is the residue of a multifunctional
12 coupling agent used in the production of the radial
13 block copolymer, and n is a number greater than 2
14 representative of the number of branches appended to
15 X.

16 pS has an average number molecular weight
17 ranging from about 10,000 to about 25,000, pI has an
18 average number molecular weight ranging from about
19 20,000 to about 70,000, (pI-pB) has an average number
20 molecular weight ranging from about 20,000 to about
21 70,000, the overall number average molecular weight
22 of the block copolymer ranges from about 90,000 to
23 about 380,000, and wherein the pS component is
24 present in an amount of at least 25 parts to about 50
25 parts per 100 parts by weight of the radial block
26 copolymer.

- 33 -

1 2. The composition of Claim 1 wherein the
2 average molecular weight of the pI or (pI+pB) compo-
3 nents of the radial block copolymer ranges from about
4 20,000 to about 40,000, the average molecular weight
5 of the pS component ranges from about 14,000 to about
6 20,000, the overall molecular weight of the copolymer
7 ranges from about 100,000 to about 240,000, and
8 wherein the pS component is present in amount ranging
9 from about 27 parts to about 45 parts per 100 parts
10 by weight of the copolymer.

1 3. A hot melt adhesive composition useful in
2 the assembly of disposable articles which comprises
3 from about 15 percent to about 35 percent
4 based on the weight of the hot-melt adhesive composi-
5 tion, of a radial block copolymer constituted of a
6 polystyrene block segment and a polyisoprene block
7 segment, or polyisoprene block segment an end of
8 which is constituted of butadiene, as characterized
9 by either of the formulas:

10 (1) (pS-pI)_nX, or

11 (2) (pS-pI-pB)_nX

12 where pS is polystyrene, pI is polyisoprene, pB is
13 polybutadiene, X is the residue of a multifunctional
14 coupling agent used in the production of the radial
15 block copolymer, and n is a number greater than 2
16 representative of the number of branches appended to
17 X,

18 pS has an average number molecular weight
19 ranging from about 10,000 to about 25,000, pI has an
20 average number molecular weight ranging from about
 20,000 to about 70,000, (pI+pB) has an average number
 molecular weight ranging from about 20,000 to about

21 70,000, the overall number average molecular weight
22 of the block copolymer ranges from about 90,000 to
23 about 380,000, and wherein the pS component is
24 present in an amount of at least 25 parts to about 50
25 parts per 100 parts by weight of the radial block
26 copolymer

27 from about 45 percent to about 70 percent
28 of a compatible primary tackifying resin, based on
29 the weight of the hot-melt adhesive composition,

30 from 0 percent to about 30 percent of a
31 plastizing oil or secondary tackifying resin, based
32 on the weight of the hot melt adhesive composition,
33 and

34 from about 0.1 percent to about 2 percent
35 of a stabilizer, based on the weight of the hot-melt
36 adhesive composition.

1 4. The composition of Claim 3 wherein the hot
2 melt adhesive composition contains from about 20
3 percent to about 30 percent of the copolymer.

1 5. The composition of Claim 3 wherein the hot
2 melt adhesive composition contains from about 50
3 percent to about 60 percent of the compatible primary
4 tackifying resin.

1 6. The composition of Claim 3 wherein the hot-
2 melt adhesive composition contains from about 5
3 percent to about 20 percent of the plasticizing oil
4 or secondary tackifying resin.

1 7. The composition of Claim 3 wherein the hot-
2 melt adhesive composition contains from about 0.5
3 percent to about 1.5 percent of the stabilizer.

- 35 -

1 8. The composition of Claim 3 wherein the
2 average molecular weight of the pI or (pI+pB) compo-
3 nents of the radial block copolymer ranges from about
4 20,000 to about 40,000, the average molecular weight
5 of the pS component ranges from about 14,000 to about
6 20,000, the overall molecular weight of the copolymer
7 ranges from about 100,000 to about 240,000, and
8 wherein the pS component is present in amount ranging
9 from about 27 parts to about 45 parts per 100 parts
10 by weight of the copolymer.

1 9. The composition of Claim 3 wherein the hot-
2 melt adhesive composition additionally contains up
3 to about 5 percent, based on the weight of the
4 hot-melt adhesive composition, of a hydrocarbon wax
5 sufficient to form an adhesive composition useful for
6 lining magazines or books, or for packaging and
7 carton sealing.

1 10. A disposable article comprising a polyethy-
2 lene or polypropylene substrate bonded to a tissue,
3 non-woven, polyethylene or polypropylene, substrate
4 using a hot-melt adhesive composition which comprises
5 from about 15 percent to about 35 percent,
6 based on the weight of the hot-melt adhesive composi-
7 tions, of a radial block copolymer constituted of a
4 polystyrene block segment and a polyisoprene block
5 segment, or polyisoprene block an end of which is
6 constituted of butadiene, as characterized by either
7 of the formulas:

- 8 (1) $(pS-pI)_nX$, or
9 (2) $(pS-pI-pB)_nX$

- 36 -

10 where pS is polystyrene, pI is polyisoprene, pB is
11 polybutadiene, X is the residue of a multifunctional
12 coupling agent used in the production of the radial
13 block copolymer, and n is a number greater than 2
14 representative of the number of branches appended to
15 X,

16 pS has an average number molecular weight
17 ranging from about 10,000 to about 25,000, pI has an
18 average number molecular weight ranging from about
19 20,000 to about 70,000, (pI-pB) has an average number
20 molecular weight ranging from about 20,000 to about
21 70,000, the overall number average molecular weight
22 of the block copolymer ranges from about 90,000 to
23 about 380,000, and wherein the pS component is
24 present in an amount of at least 25 parts to about 50
25 parts per 100 parts by weight of the radial block
26 copolymer,

27 from about 45 percent to about 70 percent
28 of a compatible primary tackifying resin, based on
29 the weight of the hot-melt adhesive composition,

30 from 0 percent to about 30 percent of a
31 plastizing oil or secondary tackifying resin, based
32 on the weight of the hot melt adhesive composition,
33 and

34 from about 0.1 percent to about 2 percent
35 of a stabilizer, based on the weight of the hot melt
36 adhesive composition.

1 11. The article of manufacture according to
2 Claim 10 wherein the hot-melt adhesive composition
3 contains from about 20 percent to about 30 percent
4 of the radial block copolymer.

- 37 -

1 12. The article of manufacture according to
2 Claim 10 wherein the hot-melt adhesive composition
3 contains from about 50 percent to about 60 percent
4 of the compatible primary tackifying resin.

1 13. The article of manufacture according to
2 Claim 10 wherein the hot melt adhesive composition
3 contains from about 5 percent to about 20 percent
4 of the plasticizing oil or secondary tackifying
5 resin.

1 14. The article of manufacture according to
2 Claim 10 wherein the hot melt adhesive composition
3 contains from about 0.5 percent to about 1.5 percent
4 of the stabilizer.

1 15. The article of manufacture according to
2 Claim 10 wherein the average molecular weight of
3 the pI or (pI+pB) components of the radial block
4 copolymer ranges from about 20,000 to about 40,000,
5 the average molecular weight of a pS component ranges
6 from about 14,000 to about 20,000, the overall
7 molecular weight of the copolymer ranges from about
8 100,000 to about 240,000, and wherein the pS compo-
9 nent is present in amount ranging from about 27 parts
10 to about 45 parts per 100 parts by weight of the
11 copolymer.

- 38 -

1 16. The article of manufacture according to
2 Claim 10 wherein the primary tackifying resin is any
3 compatible resin or mixture thereof selected from the
4 group consisting of (1) natural and modified rosins;
5 (2) glycerol and pentaerythritol esters of natural
6 and modified rosins; (3) copolymers and terpolymers
7 of natured terpenes; (4) polyterpene resins having a
8 softening point, as determined by ASTM method
9 E28-58T, of from about 80° to 150°C; (5) phenolic
10 modified terpene resins and hydrogenated derivatives
11 thereof; (6) aliphatic petroleum hydrocarbon resins
12 having a Ball and Ring softening point of from about
13 70° to 135°C; (7) aromatic petroleum hydrocarbon
14 resins, and mixed aromatic and aliphatic paraffin
15 hydrocarbon resins, and the hydrogenated derivatives
16 thereof; (8) aromatic modified alicyclic petroleum
17 hydrocarbon resins and the hydrogenated derivatives
18 thereof; and (9) alicyclic petroleum hydrocarbon
19 resins and the hydrogenated derivatives thereof.

1 17. The article of manufacture according to
2 Claim 10 wherein the disposable article is selected
3 from the group consisting of diapers, sanitary
4 napkins and bed pads.

1 18. The article of manufacture according to
2 Claim 10 wherein the adhesive component of the dispo-
3 sable article is applied as a discontinuous phase.

1 19. The article of manufacture according to
2 Claim 10 wherein the disposable article is of
3 multi-line construction.

- 39 -

1 20. The article of manufacture according to
2 Claim 19 wherein the adhesive component used in
3 forming the disposable article is applied as fine
4 parallel longitudinal strips, swirl or as a multi-
5 dot pattern of adhesive droplets.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/04334

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.C1. 5 C08F297/04; C08G81/02; C09J153/02; C09J7/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.C1. 5	C08F ; C08G ; C09J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	WORLD PATENTS INDEX LATEST Week 8327, Derwent Publications Ltd., London, GB; AN 83-702656 & JP,A,58 089 672 (JAPAN SYNTHETIC RUBBER) 28 May 1983	1-9
Y	see abstract	1-20
Y	EP,A,0 306 232 (MINNESOTA MINING AND MANUFACTURING COMP.) 8 March 1989 see page 5, line 25 - line 29; claims	1-20
X	US,A,4 096 203 (ST. CLAIR) 20 June 1978 see column 4, line 25 - line 44; claims 1-4	1-9
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
2 31 AUGUST 1992	11. 09. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	LOISELET-TAISNE S.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	WORLD PATENTS INDEX LATEST Week 8329, Derwent Publications Ltd., London, GB; AN 83-715139 & SU,A,956 532 (TRISHIN) 7 September 1982 see abstract ---	1-2
X	EP,A,0 362 850 (KURARAY CO.) 11 Apr 11 1990 see block copolymer (E) shown in Table 2 see claims 4,6; table 2 ---	1
P,A	US,A,5 028 646 (MILLER ET AL.) 2 July 1991 see column 6, line 30 - line 31; examples see column 6, line 38 - line 53; claims ---	1,3-20
A	US,A,4 163 077 (ANTONSEN ET AL.) 31 July 1979 see claim 1 ---	1,10

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9204334
SA 60795**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 31/08/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP-A-0306232	08-03-89	AU-A-	2117188	02-03-89
		JP-A-	1095175	13-04-89
		US-A-	5112889	12-05-92

US-A-4096203	20-06-78	None		

EP-A-0362850	11-04-90	JP-A-	2300218	12-12-90
		JP-A-	2102212	13-04-90
		JP-A-	2135256	24-05-90
		US-A-	4987194	22-01-91

US-A-5028646	02-07-91	US-A-	5112889	12-05-92

US-A-4163077	31-07-79	AU-B-	520187	21-01-82
		AU-A-	4609879	25-10-79
		CA-A-	1134212	26-10-82
		DE-A, C	2916054	31-10-79
		FR-A, B	2423524	16-11-79
		GB-A, B	2019416	31-10-79
		JP-C-	1398694	07-09-87
		JP-A-	54145740	14-11-79
		JP-B-	62006597	12-02-87
		NL-A-	7902904	23-10-79
		SE-B-	446272	25-08-86
		SE-A-	7903273	18-10-79
